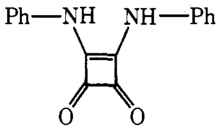
Electronic and N(1s) X-Ray Photoelectron Spectra of the 1,2- and 1,3-Dianilides of Squaric Acid

Eberhard W. Neuse* and Brian R. Green

Contribution from the Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa. Received October 2, 1974

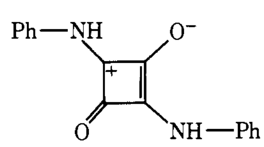
Abstract: Both 1,2-dianilinocyclobutene-3,4-dione (**2**) and its 1,3-disubstituted isomer (**3**), commonly described as 1,3-dianilinocyclobutenediylium 2,4-diolate, were investigated by electronic and X-ray photoelectron spectroscopy. The considerable red shifts of the $\pi \rightarrow \pi^*$ bands of the high-wavelength region observed relative to the simple unphenylated 1,2- and 1,3-diamides indicate participation of the nitrogen atoms in the domain of conjugation, **3** showing a larger chromophore (both phenyl groups included) than **2** (one phenyl group included). The N(1s) binding energies derived from the photoelectron spectra are the same, within experimental error, in both isomers (399.5 and 399.6 eV, respectively), their magnitudes reflecting more than 50% iminium character brought about by dissipation of electronic charge from nitrogen atoms to both the four-membered ring system and the phenyl groups. To reconcile the identity of the nitrogen atom charges with the different ir carbonyl stretching frequencies in the two compounds, canonicals with negative charge accumulated on the phenyl rings must be weighted higher in **2** than in **3**, whereas those with negative charge localized on oxygen are more stabilized, and so prevail, in **3**. The results, favoring mesoionic structures for both dianilides, disallow the conventional diketone representation (1,2-dianilinocyclobutene-3,4-dione) of **2** as the principal contributor and permit a minor contribution, at best, of the commonly used dicationic cyclobutenediylium diolate representation in the 1,3-isomer case.

Two isomeric bis(*N*-phenylamides) can be derived from squaric acid (**1**): the 1,2-disubstituted compound (**2**), commonly described[1] as 1,2-dianilinocyclobutene-3,4-dione (**2a**), and the 1,3-counterpart (**3**), which has generally been

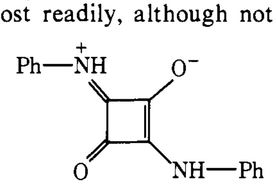


2a

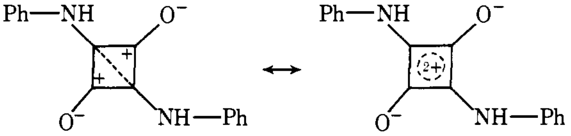
depicted[1c,2] by the mesoionic structures **3a,b** or the dicationic 1,3-dianilinocyclobutenediylium 2,4-diolate structure **3c**. The 1,2 isomer results most readily, although not exclusively,[1e] from amidation of squaric diesters, whereas the 1,3-disubstituted compound is the main product[2f] arising in the amidation of the free acid. The two types of substitution orientation in amidation reactions have recently been investigated in some detail, and possible mechanisms have been proposed.[1e,2f,g] The structural representations of **2** and **3** rest primarily on ir evidence: while **2** exhibits two (asym and sym) carbonyl stretching bands at positions (1795 and 1668 cm^{-1})[1c] suggestive of cyclic 1,2-diketones, the appreciably reduced C-O bond order in **3** results in a broad band system centered at the considerably lower frequency range of 1595-1615 cm^{-1}.[1c,3] Several observations make it quite obvious, however, that most of these representations constitute oversimplifications of the real situation in both isomers. Certain 1,2-dipyrrolyl derivatives of **1**, for example, give electronic absorption maxima (440 nm)[4a,b] far enough on the high-wavelength side to justify the structural proposal **4**



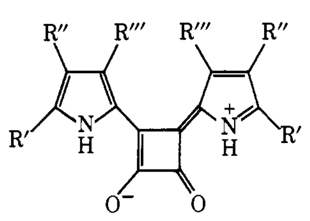
3a



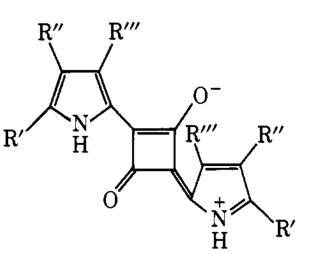
3b



3c

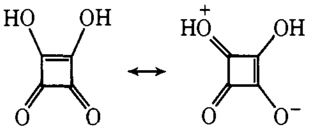


4



5

(R′, R″, R‴ = H and alkyl)[4a,b] with δ^- localized on 0 and $\delta+$ accumulated on N. This indicates a C-O π bond order effectively lower than unity in such compounds that allow for π-conjugative participation of the substituents and include even squaric acid itself, for which a Pariser-Parr-Pople MO calculation,[5a] supported by an X-ray analysis,[5b] suggests a C-O π bond order of 0.862 in accord with a 28% contribution by monohydroxonium structures.



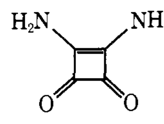
1

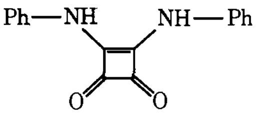
In light of these findings appreciable contributions by analogous isoelectronic iminium structures should be expected in **2** as well, a conclusion supported by the virtually identical C-O π bond orders in **1** and **2** inferred from the nearly coincident algebraic means of the asym and sym C-O stretching bands (1732 and 1730 cm^{-1} in **1** and **2**, respectively).[6]

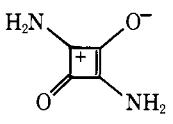
Further, judging from the low-frequency position of λ_{max} in certain 1,3-dipyrrolyl derivatives of **1** (554-560 nm),[4a,c] for which accordingly the mesoionic structure **5** (R′, R″, R‴ = H and alkyl) has been suggested,[4] a delocalization pattern as depicted by **3b** can be inferred for the 1,3-dianilino compound; to this canonical, thus, major importance should be attributed at the expense of **3a**.

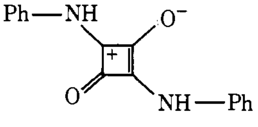
It should, finally, be borne in mind that a successful synthesis of 1,3-disubstituted derivatives of squaric acid requires the substituents to be capable of accepting positive charge with an efficiency greater than that shown by simple hydroxy or alkoxy groups.[7] Amino groups, possessing a

Table I. Electronic Spectra ($\pi \rightarrow \pi^*$ Transitions) of Some 1,2- and 1,3-Diamides of Squaric Acid


6


2


7


3

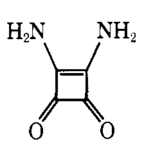
Compd	Medium	λ_{max}, nm (ϵ)[a]		Lit.
6	1 *M* HCl	253 (97%)	275 (100%)	lb
	1 *M* H_2SO_4[b]	260 sh (29,000)	278 (36,000)	This work
	KBr[c]	255 sh	287	This work
2	1 *M* HCl	303 sh (90%)	327 (100%)	lb
	1 *M* H_2SO_4[d]	~312 sh (36,500)	342 (47,000)	This work
	KBr[c]	305	340 sh	This work
7	1 *M* H_2SO_4[b]	260	285	This work
	KBr[c]	260	293	This work
3	1 *M* H_2SO_4[e]		388 (66,000)	This work
	KBr[c]		368	This work

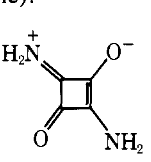
[a] Relative intensities in 1 *M* HCl solution experiments. [b] Solute concentration, 9×10^{-5} mol l.$^{-1}$. [c] Sample concentration in disk, 0.01% by weight. [d] Solute concentration, 3.8×10^{-6} mol l.$^{-1}$. [e] Solute concentration, 3.8×10^{-5} mol l.$^{-1}$.

more powerful donor center, fulfill this requirement,[8] thereby stabilizing the mesoionic 1,3-disubstituted ring system sufficiently to ensure its existence. This experimental experience places structures with a dipositive four-membered ring system of the type **3c** in a dubious light,[9] as such structures lack the operation of mechanisms that would result in the required withdrawal of positive charge from that ring.

In connection with studies of polymeric squaryl amides[10] we were interested in a more realistic assessment of the relative importance of contributing canonicals in both 1,2- and 1,3-diamides of **1**. This prompted an examination of the electronic and X-ray photoelectron (ESCA) spectra of the two isomers **2** and **3** chosen here as representative model compounds.

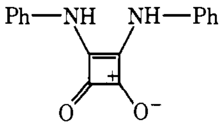
1,2-Bis(*N*-phenylamide) (2). The electronic spectrum of **2** was first reported by Webb's group.[1b] These workers used water, dilute aqueous alkali, and dilute (1 *M*) aqueous HCl as solvents. Anion formation (deprotonation) was suspected in both water and alkali solutions, but can be neglected in the dilute acid medium, which probably dissolves the amide without either protonation or deprotonation.[11] Solubility problems prevented the authors from determining the extinction coefficients; the maxima were merely labeled with relative intensity values. The results are reproduced in Table I, which also contains data on the simple 1,2-diamide **6** (1,2-diaminocyclobutene-3,4-dione).[12]

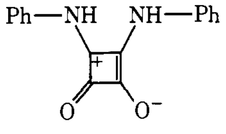

6

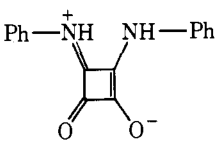

7

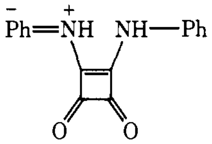
We recorded the spectra of both **2** and **6** in dilute (1 *M*) aqueous H_2SO_4. This medium presented no solubility problems at the low substrate concentration (~10^{-5} mol l.$^{-1}$) employed and so enabled us to obtain quantitative intensity data. Absorption patterns were similar to those[1b] in 1 *M* HCl, although somewhat red shifted in the case of **2**. We also recorded the spectra in a KBr matrix. This medium, while disallowing quantitative intensity determinations because of erratic base-line variations, gave reproducible λ_{max} positions; it offered the advantage of avoiding uncertainties in the amides' protonation-deprotonation behavior in solution. Our results for **2** and **6** in both media are given in Table I.

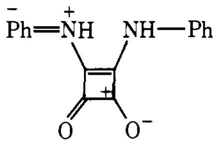
The tabulation reveals distinct bathochromic and hyperchromic shifts in the solution spectra as one goes from the simple diamide to the dianilino compound. The same trend in λ_{max}, albeit less pronounced in degree, is apparent in the solid-state spectra. An extended domain of conjugation, exceeding that in, e.g., 1,2-diphenylcyclobutene-3,4-dione,[13] clearly exists in **2** relative to the unphenylated **6**. As the tetrahedrally hybridized N atoms in the diketonic form **2a** prevent π overlap between phenyl groups and cyclobutene ring, compound **2**, if solely or predominantly represented by **2a**, should give absorption maxima close in position and intensity to those exhibited by **6**. The observed strong red shift (and intensity enhancement) in **2** relative to **6**, therefore, immediately eliminates **2a** (and, by the same argument, **2b,c**) as the most important contributing resonance form in **2**. On the other hand, it clearly permits appreciable contributions from such forms as **2d–h**, in which trigonal hybridization on N allows for optimal molecular planarity and π overlap, a situation comparable to that in protonated azomethines;[14] thus, in **2d**, **2e**, **2g**, and **2h**, conjugation can readily extend from a carbonyl oxygen atom to the phenyl group of the diagonally attached anilino substituent. Forms **2e–h** with partial negative charge on the benzene rings de-

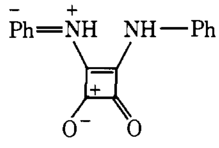

2b


2c


2d


2e


2f


2g

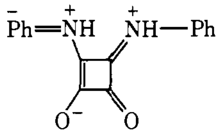

2h

Table **II.** N(1s) Binding Energy and Atomic Charge Parameter of Dianilides 2 and 3

Compd	No. of experiments	E_b, eV[a]	E_b, eV[b] (ultimate value)	q_N[c]	Iminium structure,[d] %
2	4[e]	399.40[f,g]	399.5	+0.02	58
	2[h]	399.825[g,i]			
3	4[e]	399.475[f,g]	399.6	+0.04	60
	2[h]	399.75[g,i]			

[a] From eq 2; precision, ±0.2 eV; estimated accuracy, ±0.7 eV. [b] Average of two values from preceding column, weighted by number of experiments and rounded to one decimal place. [c] From E_b of preceding column by means of Siegbahn's correlation (ref 15). Precision, ±0.04. [d] See text and ref 25. Precision, ±7. [e] Performed on ES 200 (Al Kα radiation) at ambient temperature. [f] Calibrated against both NH_4NO_3 and $NaNO_3$. [g] All NH_4NO_3-standardized spectra referenced against both ammonium N and nitrate N and averaged. [h] Performed on ES 100 (Al Kα radiation) at −100°. [i] Calibrated against NH_4NO_3.

Table **III.** Calculated Nitrogen Atom Charge Parameter[a] of Selected Canonicals of 2 and 3

Canonical	q_N	Canonical	q_N
2a	−0.30	3a	−0.275
2b	−0.30	3b	−0.025
2c	−0.275	3c	−0.30
2d	−0.025	3d	−0.30
2e	−0.025	3e	−0.025
2f	−0.025	3f	0.00
2g	−0.025	3g	−0.025
2h	+0.25	3h	+0.25

[a] Calculated by Siegbahn's approach (see text).

rive some probability of contribution from the analogous situation in aniline. For this aromatic amine, some 54% iminium structure was convincingly demonstrated several years ago by Siegbahn's group[15] on the basis of ESCA results. Form **e**, comprising the lowest degree of charge separation (and lacking the unfavorable dipole interaction existing especially in **f**), can be predicted to prevail over forms **f** and **g** despite the stabilizing influence of the homoallylic cation core in the latter two.[16] Given a ground-state C–O π bond order for **2** similar to that in **1**, the sum of forms like **2b–d,f,g** with partially polarized carbonyl groups can be assigned a weighting factor greater than one-third that of the diketone structures **2a** and **2e** (and similar, less important canonicals). This suggests that the reduced importance of **2a** is largely compensated for by **2e.**

The atomic charge on N varies considerably within the range of contributing forms in **2.** Given a predominant ground-state contribution by **2d** and **2e,** and a less important one by **2a,** one would expect the hybrid structure of **2** to carry an atomic charge on each N atom close to the arithmetic mean of the nitrogen atom charge in an sp^3-hybridized aromatic amine and that in a corresponding iminium salt in which the heteroatom has donated its nonbonding electron pair so as to create a formal double bond to one of the substituents. Determination of the nitrogen atom charge,[15] q_N, in **2** by X-ray photoelectron spectroscopy enabled us to verify this expectation. ESCA permits the measurement of core-electron binding energies, E_b (that is, energy differences between Fermi level and 1s atomic levels), from the relation in eq 1, where $E_{h\nu}$ is the incident X-ray

$$E_b = E_{h\nu} - E_{kin} - \Phi_{sp} \tag{1}$$

photon energy, E_{kin} is the measured photoelectron kinetic energy, and Φ_{sp} is the work function of the spectrometer material.[18] Existing correlations in the literature[19] then allow the determination of the atomic charge from E_b so obtained.

In the present work, the N(1s) binding energy of **2** was determined by recording the ESCA spectrum of the solid compound in the presence of ammonium nitrate as internal standard. A second series of experiments utilized sodium nitrate for reference. The binding energies of the two nitrogen atoms in the first standard ($E_{b(NH_4NO_3)}$ = 402.3 eV; $E_{b(NH_4NO_3)}$ = 407.2 eV) are known from Hendrickson's work,[19c,d] whose results in turn rest on calibration against Siegbahn's earlier series of nitrogen-containing compounds.[19b] The binding energy of the second standard ($E_{b(NaNO_3)}$ = 407.2 eV) is available directly from Siegbahn's paper.[15] This internal standard technique, permitting calculation of E_b from eq 2, circumvents the measurement of Φ_{sp}[20] and renders our findings directly comparable with Siegbahn's work.[15] A total of six spectra, induced with Al Kα radiation ($E_{h\nu}$ = 1486.6 eV), were scanned on two different instruments (see Experimental Section). In calculating $E_{b(2)}$ from measured $E_{kin(2)}$ and $E_{kin(standard)}$ by eq 2, we used all nitrogen types of the standards. The results were averaged as indicated in Table II, giving a final value[21] of $E_{b(2)}$ = 399.5 eV.

$$E_{b(standard)} - E_{b(unknown)} = E_{kin(unknown)} - E_{kin(standard)} \tag{2}$$

Entering $E_{b(2)}$ so obtained in Siegbahn's E_b–q_N correlation,[15] we find a nitrogen atom charge, $q_{N(2)}$, of +0.02. Siegbahn's calculation[15,19b] of q_N values used in that correlation is based on a method utilizing Pauling's partial ionic character, I, of the bonds extending from the N atom under consideration. The charge parameter q_i on nucleus i (here N) can be expressed as

$$q_i = Q_i + \sum_{j \neq i} I_{ij} \tag{3}$$

where Q_i is the formal charge on nucleus i, and I_{ij} for bond i–j is given by eq 4, χ_i and χ_j being the electronegativities

$$I_{ij} = 1 - e^{-0.25(\chi_i - \chi_j)^2} \tag{4}$$

of nuclei i and j participating in the bond i–j. Using electronegativities calculated by Pauling's method for the nuclei (N, N$^+$, C, C$^+$) involved, we computed q_N for canonicals **2a–g**,[22] as well as for the representative form **2h** possessing two formally unipositive N atoms. The results are compiled in Table III.

Interpolation of the experimental $q_{N(2)}$ between the calculated $q_{N(2a)}$ and $q_{N(2h)}$ shows the hybrid structure of **2** to comprise some 58% iminium character. Forms **2d–g** can at best provide 50% total iminium structure. Since the diamine structure **2a,** although less important, cannot be neglected as a ground-state contributor, this indicates that an appreciable weight must be assigned to a structure such as **2h** (despite some additional destabilization caused by the mutually repelling iminium centers), to compensate for the contribution of **2a** and provide the extra 8% iminium character required by the ESCA results.[23]

On balance, then, we are led to conclude from the spectroscopic data presented that the 1,2-dianilino compound, far from being depicted by **2a,** represents a mesoionic system exhibiting considerable charge separation, canonicals with one and even two formally unipositive charges on the nitrogen atoms carrying major weight.

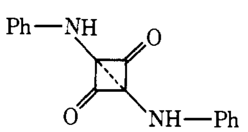
1,3-Bis(*N*-phenylamide) (**3**). The electronic spectra of **3** and, for comparison, of the unphenylated 1,3-diamide **7**[1d] were recorded as before on both 1 *M* H_2SO_4 solutions and KBr disks. The $\pi \rightarrow \pi^*$ absorption maxima are given in Table I. Furthermore, the ESCA spectrum of **3** was taken on the solid compound (six experiments) and evaluated as in the case of **2**, giving $q_{N(3)}$ = +0.04 (Table II). The results and pertinent inferences can be stated as follows.

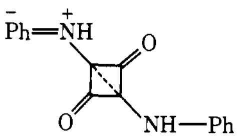
(i) No substantial bathochromic effect is noticed on going from the simple 1,2-diamide **6** to the corresponding 1,3-isomer **7**, a reasonable finding in view of the approximately equal length of the optimally attainable conjugated domains (N-C-C-C-O and N-C-C-C-N) in both compounds.

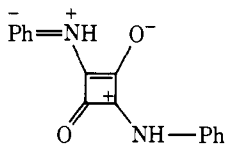
(ii) In contrast, the 1,3-dianilide **3** gives λ_{max} considerably red shifted and intensified relative to the 1,2-isomer **2**. This shows that, taken together, those canonicals providing the largest possible chromophores[24] carry a higher weight in **3** than in **2**.

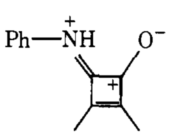
(iii) The degree of iminium character[25] as reflected in the atomic charge parameter is the same, within experimental error, in both isomers **2** and **3**. This result surprises, as one would intuitively predict the weight of charge-separated canonicals in **3**[26] to be higher than in **2**; it indicates that the extended chromophore in **3** (relative to **2**) is for the most part associated with **3h**, which, although possessing the same percentage iminium structure as the **2h** counterpart, comprises a longer domain of π overlap (both phenyl groups incorporated). The ESCA results, by implication, also suggest the combined contribution of canonicals with sp^3-hybridized N (**3a,c,d**) to be about the same as that of forms **2a–c** in the 1,2 isomer. Since ir evidence accords with a C–O π bond order (about 0.5[4c,27]) distinctly lower than in **2** (about 0.8[5]), **3d,e** must be appreciably less important than counterparts **2a,e**, a conclusion which appears not unreasonable in light of the required cross-ring bonding[28] in the former two canonicals. In order to comply with the ESCA results, **3a**, compensating for the decreased importance of **3d**, must then assume a weighting factor approximately comparable to that of **2a** and well in excess of that of its counterparts **2b,c**. This is in fact what one would expect on the basis of the enhanced resonance stabilization imparted to **3a** (4 degenerate forms) relative to **2b,c** (2 × 2 degenerate forms).

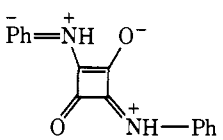
While one might also invoke **3c** (competing with **3g**) in order to rationalize the diminished π bond order, major importance of this diylium form, which excludes both anilino groups from effective conjugation, would be in contradiction to the λ_{max} observed and hence cannot be postulated. It rather appears that the contribution of **3g** is quite adequate to offset the very minor weight of forms **3d,e** with unity C–O π bond order.


3d


3e


3f


3g


3h

In summary, then, we find **3** to comprise a mesionic system possessing the same charge density on N as observed in **2**. The lower C–O π bond order (in relation to **2**) evidenced ir spectroscopically derives from predominant ground-state contributions of ketoenolate and iminium diolate structures, and the extended chromophore, reflected in the high-wavelength $\pi \rightarrow \pi^*$ maximum, can be accounted for in terms of major contributions by a number of iminium structures including a bisiminium ketoenolate with both phenyl groups comprised by the conjugated domain.[29] On the other hand, we find no basis for ascribing major importance to the cyclobutenediylium diolate form with a dipositive four-membered ring.

To avoid cumbersome multistructural representations, we shall henceforth, for convenience, use the conventional diketone structure **2a** and the ketoenolate structure **3a** for the two dianilides, although most certainly neither formula, neglecting existent iminium character, reflects the electronic distribution in the two isomers to a prevalent extent.

Experimental Section

Compounds. Both dianilides **2** and **3** were prepared as described.[1c,e] Diamide **6**, synthesized by a literature[12] procedure, was recrystallized from *N,N*-dimethylformamide. The isomer **7** was prepared by a previously described method,[1d] except that the heating time was reduced to 1 min to prevent excessive degradation; recrystallization from dimethyl sulfoxide furnished the compound in analytical purity. The ir spectra of both **6** and **7** conformed to those reproduced in the literature.[1d]

Instrumental Techniques. Ir spectra (KBr disks) were taken on a Perkin Elmer, Model 521, spectrometer. Electronic spectra were recorded on a Unicam SP 1800 ultraviolet spectrophotometer in the 250–450 nm region, with solute concentrations as stated in Table I. The KBr disks for electronic spectroscopy were pressed to 0.25 ± 0.02 mm thickness to reduce background scattering and ensure reasonable base line constancy. ESCA spectra (Al Kα radiation) were obtained on AEI Scientific ES200 and ES100 photoelectron spectrometers at ambient temperature and $-100°$ (10^{-6} Torr) (see Table II) in the laboratories of the Applied Physics Division, Bayer AG, Leverkusen, and the Chemistry Department, Northwestern University, Evanston, Ill.; samples were spread in powder form on gold-plated 6 × 13 mm probes.

Acknowledgment. This work was supported by the Council for Scientific and Industrial Research and by the Atomic Energy Board. One of us (B.R.G.) acknowledges the bursary support given by the National Institute for Metallurgy. We are deeply indebted to Dr. R. Holm, Bayer AG, for his most kind cooperation in recording a large number of ESCA spectra under variable conditions of standardization, and to Drs. J. Lambert and C. D. McLaughlin, Northwestern University, who obligingly recorded some of the spectra referenced against ammonium nitrate.

References and Notes

(1) (a) G. Maahs and P. Hegenberg, *Angew. Chem.*, **78**, 927 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 888 (1966); (b) G. R. Griffiths, M. D. Rowe, and G. A. Webb, *J. Mol. Struct.*, **8**, 363 (1971); (c) J. Gauger and G. Manecke, *Chem. Ber.*, **103**, 2696 (1970); (d) *ibid.*, **103**, 3553 (1970); (e) E. Neuse and B. Green, *Justus Liebigs Ann. Chem.*, 619 (1973).

(2) (a) H.-E. Sprenger, German Patent Application C 41650 IV b/120 (1967); German Offen. 1618211 (1971); (b) G. Manecke and J. Gauger, *Tetrahedron Lett.*, 3509 (1967); 1339 (1968); (c) H.-E. Sprenger and W. Ziegenbein, *Angew. Chem.*, **80**, 541 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 530 (1968); (d) G. Manecke and J. Gauger, *Makromol. Chem.*, **125**, 231 (1969); (e) J. Gauger and G. Manecke, *Angew. Chem.*, **81**, 917 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 898 (1969); (f) E. W. Neuse and B. R. Green, *Justus Liebigs Ann. Chem.*, 633 (1973); (g) E. W. Neuse and B. R. Green, *J. Org. Chem.*, **39**, 3881 (1974).

(3) This high-intensity absorption, generally in the 1500–1600 cm^{-1} region in 1,3-disubstituted squaric acid derivatives, probably derives from C–C and C–O stretching modes of the entire "quasiaromatic" cyclobutenonolate ring system.[1c,2b,d,4]

(4) (a) A. Treibs and K. Jacob, *Justus Liebigs Ann. Chem.*, **699**, 153 (1966); (b) *ibid.*, **712**, 123 (1968); (c) A. Treibs, K. Jacob, and R. Tribollet, *ibid.*, **741**, 101 (1970).

(5) (a) S. Skujins and G. A. Webb, *Spectrochim. Acta, Part A*, **25**, 917 (1969). These authors also calculated p_{C-O} by a HMO method, obtaining the somewhat lower value of 0.715. However, since the HMO approach tends to overemphasize the ionic character, choice of the P–P–P results for the purpose of this discussion appears more appropriate. (b) D. Semmingsen, *Tetrahedron Lett.*, 807 (1973).

(6) (a) In the ideal case of a linear molecule Y–X–Y, the root-mean-square of frequencies ν_3 (asym, higher) and ν_1 (sym, lower) is approximately equal to the frequency of the isolated X–Y bond stretching mode.[6b] Adopting this model in the present case, we use the algebraic mean of ν_3 and ν_1, as this is generally not very different from the weighted rms of the two frequencies. (b) P. Gans, "Vibrating Molecules", Chapman and Hall, London, 1971, Chapter 7.

(7) Thus, while 1,3-bisresorcinol and -bisphloroglucinol derivatives of **1** have been prepared,[4a] simple dialkoxy derivatives (squaric diesters), just like the free acid proper, are known to exist exclusively as 1,2 compounds, indicating that considerable additional delocalization is required to render the oxonium system efficacious in 1,3-isomer stabilization.

(8) (a) An example of the highly stabilized tetraamino-substituted cyclobutenediylium cation has been provided.[8b] An interesting analogy is found in cyclopropenylium cation chemistry: triaminocyclopropenylium salts are stable enough to allow recrystallization from water,[8c] whereas the corresponding trialkoxycyclopropenylium salts are unstable, undergoing ring opening under these conditions.[8d] (b) S. Hünig and H. Pütter, *Angew. Chem.*, **85**, 143 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 149 (1973); (c) Z. Yoshida and Y. Tawara, *J. Am. Chem. Soc.*, **93**, 2573 (1971); (d) E. V. Dehmlow, *Angew. Chem.*, **86**, 203 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 209 (1974).

(9) For comparison, the total positive charges on the four-membered ring of the similarly delocalized systems, squarate dianion and phenylsquarate anion, were calculated[9b] (HMO) to be 0.944 and 1.036, respectively, and a ring charge of +1.144 was computed[9c] for the tetraphenylcyclobutenediylium cation. (b) R. West and D. L. Powell, *J. Am. Chem. Soc.*, **85**, 2577 (1963); (c) G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970).

(10) (a) B. R. Green and E. W. Neuse, *Polymer*, **14**, 230 (1973); (b) E. W. Neuse and B. R. Green, *ibid.*, **15**, 339 (1974).

(11) In more strongly protonating media both **2** and **3** are protonated, and the electronic spectra are then no longer representative of the true structures of the compounds. The considerable red shifts observed in, e.g., 9 *M* H_2SO_4 show protonation to occur on oxygen, for only this can result in an extended domain of π overlap through stabilization of such structures as **2d**, **2f**, and **2g**; N protonation, in contrast, would invariably enhance sp^3 hybridization on N, reducing the importance of **d–g**. The situation is analogous to that in open-chain vinylogous amides (enamino ketones), which are generally protonated on oxygen: G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **30**, 1407 (1965).

(12) S. Cohen and S. G. Cohen, *J. Am. Chem. Soc.*, **88** 1533 (1966).

(13) The compound gives λ_{max}(acetonitrile) = 318 nm: A. T. Blomquist and E. A. LaLancette, *J. Am. Chem. Soc.*, **83**, 1387 (1961).

(14) (a) The $-CH{=}N^+H-$ grouping in protonated aromatic azomethines provides optimal coplanarity of C=N double bond and substituent rings, as the nonbonding electron pair on N is no longer available for donation into the N-attached substituent group. Accordingly, *N*-benzylideneaniline with noncoplanar benzene rings, absorbing at 262.5 nm in cyclohexane[14b] (inflexion at 310 nm in ethanol[14c]), shows λ_{max} = 335 nm in concentrated H_2SO_4,[14b,c] in which it exists in the protonated all-planar form. (b) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Am. Chem. Soc.*, **93**, 586 (1971); (c) P. Brocklehurst, *Tetrahedron*, **18**, 299 (1962).

(15) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1968).

(16) The well-documented stability of cyclobutenylium cations[17] most certainly derives from electronic 1,3 cross-ring interaction (overlap of 2p atomic orbitals on C-1 and C-3 of the allylic structure). From spectroscopic data on cyclobutenylium cations Katz and Gold[17a] derived an HMO 1,3 π resonance integral of 0.33β, suggesting such 1,3 π interaction to be appreciable in these carbenium ion systems.

(17) (a) T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.*, **86**, 1600 (1964); (b) T. J. Katz, J. R. Hall, and W. C. Neikam, *ibid.*, **84**, 3199 (1962); (c) H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); (d) W. Ried and R. Lantzsch, *Justus Liebigs Ann. Chem.*, **756**, 173 (1972); (e) G. Seitz and H. Morck, *Chimia*, **26**, 368 (1972); (f) R. Weiss and S. Andrae, *Angew. Chem.*, **86**, 276 (1974).

(18) (a) See, for example, A. D. Baker and D. Betteridge, "Photoelectron Spectroscopy", Pergamon Press, Elmsford, N.Y., 1972. An excellent up-to-date survey of recent developments in the field is available,[18b,c] and ESCA instrumentation has been discussed.[18d] (b) H. G. Fitzky, D. Wendisch, and R. Holm, *Angew. Chem.*, **84**, 1037 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 979 (1972); (c) R. Holm, *GIT Fachz. Lab.*, **17**, 929, 1025 (1973); (d) C. A. Lucchesi and J. E. Lester, *J. Chem. Educ.*, **50**, A205 (1973).

(19) (a) For the N(1s) case, E_b–q_N correlations have been established by Siegbahn's school[15,19b] and later by Hendrickson et al.[19c,d] (b) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Ups.*, Ser. IV, **20** (1967); (c) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968); (d) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

(20) The approach chosen requires an identical Fermi level of both standard and sample. This approximation, which has been accepted by most workers in the field, is considered valid in the present case, as we are concerned entirely with relative values based on the same scale.

(21) (a) An independent calibration approach involving C(1s) reference (E_b = 285.0 ± 0.4 eV[19b,21b]) gave an $E_{b(2)}$ value higher by 0.8 ± 0.3 eV. However, the reduced precision experienced prompted us to disregard this result. (b) B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **1**, 286 (1970).

(22) Forms possessing a positive charge on the four-membered ring can be described as their allylic counterparts with the plus charge localized on a ring carbon bearing an N atom. In that case, Siegbahn's approach of calculation leads to a more positive q_N. While this has no significant effect in the case of formally uncharged N (for example, $q_N = -0.27_5$ for **2c**, the allylic counterpart of **2b**), a major change would result in forms with positively charged N ($q_N = +0.02$ for the allylic counterpart of **2f**). However, on account of their low importance caused by repulsion of the adjacent charge centers, such allylic counterparts have been disregarded in this discussion.

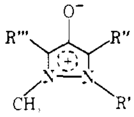
(23) Attempts to verify the dissipation of negative charge into the phenyl ring (forms **2e–h**) by C(1s) photoelectron spectroscopy met with failure, as the instrument's resolving power proved insufficient to separate peaks due to different carbon species from the very broad (half-width 3.0 ± 0.3 eV) C(1s) band system. Use of Mg Kα radiation (1253.6 eV) did not improve resolution satisfactorily.

(24) These include **2d,e,g,h** in the 1,2-dianilide case and **3b,g** in the 1,3-dianilide case, each comprising in its chromophore one phenyl group and two heteroatoms in 1,3 disposition on the four-membered ring, and additionally they include **3h** comprising the second phenyl group as well.

(25) Evaluated for **3** by interpolation of $q_{N(3)}$ between $q_{N(3a)}$ and $q_{N(3h)}$ (Table III).

(26) For example, there are 4, 8, and 4 degenerate forms of **3b**, **3f**, and **3h**, respectively, as against 2, 4 pairs of 2, and 2 such forms, respectively, of the counterparts **2d**, **2f** and **2g** (the latter including here the allylic forms with plus charge in the ring adjacent to positively charged N), and **2h**.

(27) In the mesoionic diazolium system (R′–R‴ = methyl, phenyl), the still lower C–O bond order is reflected in a stretching band position as low as 1546 cm^{-1} (DMSO): M. J. Nye, M. J. O'Hare, and W.-P. Tang, *Chem. Commun.*, 402 (1973).



(28) (a) Nonbonded electronic cross-ring interaction in four-membered cyclic β-ketoenolates was suggested[28b] by MO calculations, delocalization energies higher by 0.3–0.8β resulting from inclusion, as against neglect, of such interaction. A similar extent of 1,3 π interaction is likely to exist in cyclobutenylium cations.[17a] (b) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 1793 (1960).

(29) As all major contributing canonicals can be represented by a larger number of isoenergetic forms than is possible in the 1,2-isomer case, we conclude qualitatively that **3** is thermodynamically more stable than **2**. Efforts in this laboratory to determine the heats of formation of the two isomers by calorimetry proved inconclusive, as the results on the statistically insufficient number of experiments were within the error range of ±22 kJ mol^{-1}.